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Submitted to the Journal of Physical Chemistry

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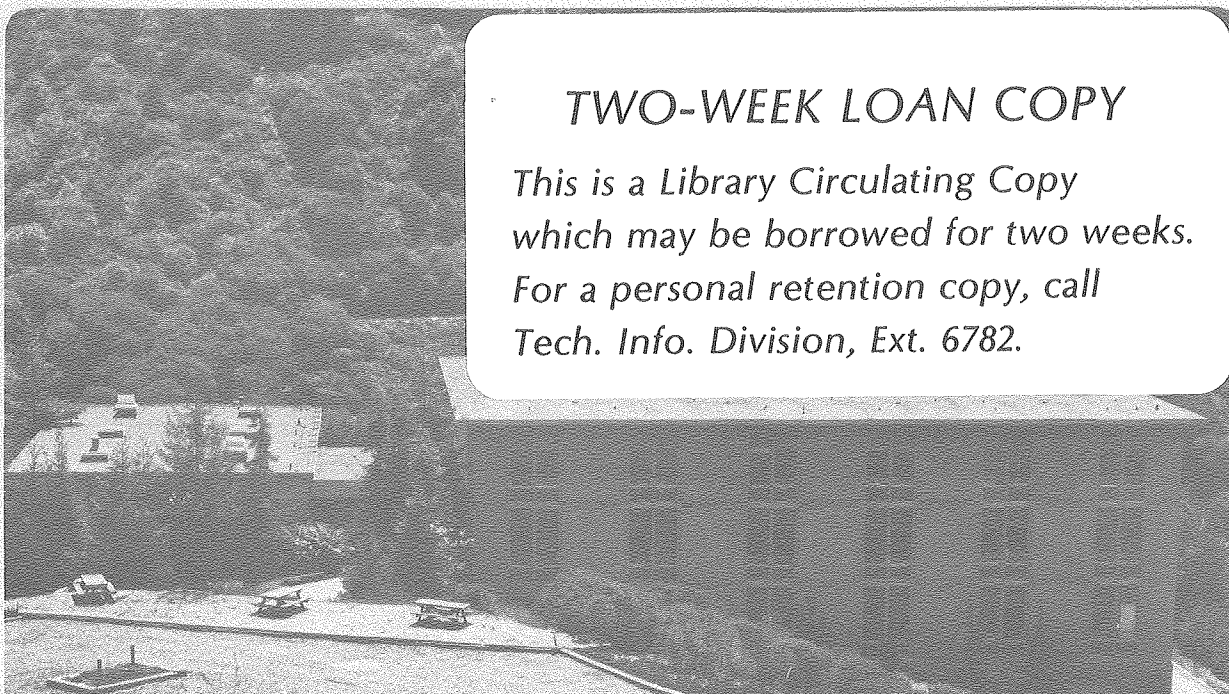
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January 1980

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Rate Constant for the Reaction $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$

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January 1980

Abstract

By use of tunable laser flash photolysis and resonance fluorescence to detect primary products, the rate constant for the reaction $O(^3P_J) + NO_2 \rightarrow O_2 + NO$ has been measured. A value of $k = 1.03 \pm .01 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$ was obtained at 296 K, which is a factor of 1.1 faster than the currently recommended value. The present work utilized in situ measurement of NO_2 via laser induced fluorescence and generated oxygen atoms from five sources.

1. Introduction

During the course of a separate study to determine absolute atomic oxygen quantum yields from the photolysis of NO_3 and N_2O_5 ,¹ a substantial amount of data was also accumulated on the reaction rate of $\text{O}(^3\text{P}_J)$ with nitrogen dioxide



This reaction has been repeatedly investigated in the past.²⁻¹¹ The recently recommended value¹² is derived from studies by Davis et al.,² Bemand et al.,¹⁰ and Slanger et al.¹¹

$$k_1(298 \text{ K}) = 9.3 \pm 0.93 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad . \quad (2)$$

There is very little or no dependence of this rate on temperature, although a slight negative temperature coefficient may be present. In this study, atomic oxygen was produced by tunable laser flash photolysis of different oxides of nitrogen, and the decay of atomic oxygen was followed as a function of time by observation of its resonance fluorescence. Experiments were carried out in an excess of N_2 at 10 torr pressure and at 296 K.

2. Experimental

The use of resonance fluorescence to detect oxygen atoms in pseudo first-order kinetic studies is well established.^{2,10,13,14} A complete description of the apparatus used for this experiment has been given elsewhere, and only the general features will be described here. The photolytic source is a pulsed frequency-doubled dye laser (Phase-R,

Model 2100B) capable of producing 1 to 2 joules of visible light or 6 to 10 millijoules of near ultraviolet radiation in a 400 ns long pulse. Wavelength measurements were made by passing a small portion of the laser beam through a one-meter grating monochromator to a Princeton Applied Research optical multichannel analyzer with a resolution of 0.04 nm. The laser beam passed into a photolysis cell of 10 cm length. At right angle to the laser beam there was an atomic oxygen resonance lamp, constructed to minimize self-reversal of the atomic oxygen triplet, $^3S_1 - ^3P_{2,1,0}$, at 130.2, 130.5, and 130.6 nm. A microwave discharge through a slow flow of ultra pure helium was found to produce the optimum signal relative to various mixtures of O_2 in argon or helium. Resonance radiation was detected at right angles to both the laser beam and the oxygen resonance lamp. The resonance radiation passed through a series of baffles and a CaF_2 filter onto a cesium iodide vacuum-ultraviolet photomultiplier tube, operated in photon counting mode. The fluorescent signal was stored in a multichannel analyzer with time intervals of 20 μs in each channel. Between 500 and 1000 laser flashes were superimposed to generate one average kinetic decay curve. Baseline subtraction and data interpretation were carried out with an on-line minicomputer, PDP/8L.

Atomic oxygen was produced from several different sources: A. Photolysis of NO_3 with relatively low energy pulses of visible light was the principal source. B. In some cases, N_2O_5 was photolyzed at 290-300 nm. C. NO_2 was photolyzed in the system, $N_2O_5 \rightleftharpoons NO_2 + NO_3$, at 351.8 nm. D. Pure NO_2 in N_2 was photolyzed at 351.8 nm at very low, 10^{-4} , conversion fractions. E. Two-photon photolysis of pure NO_2 in N_2 was also used at wavelengths between 470 and 585 nm.

The photochemical reactants were carried by 10 torr of N_2 in a flow system at 296 K. Typically the flow system included about 10 mtorr of freshly vaporized N_2O_5 in equilibrium with its decomposition products of about 1 mtorr NO_2 and 0.1 mtorr NO_3 . The N_2O_5 was synthesized by reacting purified NO_2 with an excess of O_3 in an O_2 stream, and it was stored in the dark at 196 K prior to use.

The concentration of N_2O_5 in the flowing stream was determined by a Beckman IR-7 infrared spectrophotometer, and it was always found that HNO_3 was present at about 5 percent of the N_2O_5 concentration. Either before or after flowing through the photolysis cell, the concentration of NO_2 was determined from its fluorescence as excited by a Liconix 401 He-Cd laser. Careful consideration was given to this measurement, because it is critical in determining an accurate rate constant. The threshold for detecting NO_2 with signal-to-noise equal to one was 10^9 molecules cm^{-3} for 1000 seconds of integration time. Measurements were made with 50 seconds of integration time, under which conditions 10^{11} molecules cm^{-3} were determined to 10 percent precision at the 95 percent confidence level. Response of the NO_2 analysis system was demonstrated to be linear up to 3×10^{15} molecules cm^{-3} . Measurements were made with NO_2 in the range of 1×10^{13} to 5×10^{14} molecules cm^{-3} . The sensitivity of the method was checked during and after each experiment using a standardized mixture in a tank with 115 parts per million of NO_2 in N_2 . The concentration of the tank mixture was periodically measured in a Cary 118C spectrophotometer at 400 nm wavelength and in a cell with 296 cm optical path length under conditions where corrections for N_2O_4 were negligible. The spectrophotometer was calibrated using eight separate samples of

variously purified NO_2 . A slow flow of gas was maintained to equilibrate NO_2 loss to the walls and the total pressure was measured with an MKS Baratron capacitance manometer. Over the period of runs, the molefraction of this calibration standard was constant to better than 2 parts per million.

3. Results

The flash produces an initial distribution of atomic oxygen in about 0.4 μs . The oxygen atoms within the zone of observation decay primarily due to three processes



From published values of k_1 ¹² and k_3 ¹⁵ and knowledge of the concentrations of NO_2 and NO_3 in this system, one can estimate the order of magnitude of the relaxation times associated with the chemical reactions. It is about 1 ms for reaction (1) and about 50 ms for reaction (3); the maximum contribution of reaction (3) to the decay of atomic oxygen during any single run was 5 percent; and it was usually much less than this. From simple consideration of the rate of diffusion processes, the relaxation time for atomic oxygen loss to the observation port by diffusion was estimated to be about 10 ms. From these considerations, the data were stored as photon counts in bins 20 μs wide up to a total of 20 ms.

The rate of change of atomic oxygen is

$$-\frac{d[O]}{dt} = (k_1[NO_2] + k_3[NO_3] + k_D)[O] \quad (5)$$

Experiments were carried out under conditions where the counts per second C were directly proportional to the concentration of atomic oxygen

$$[O] = FC \quad (6)$$

Although the proportionality factor was evaluated in order to obtain absolute quantum yields,¹ it is not needed to obtain rate constants under these conditions of pseudo first order kinetics. Substitution of (6) in (5) leads to cancellation of F , and the integrated rate equation is

$$\ln C = \ln C_0 - t/\tau \quad (7)$$

$$1/\tau = (k_1[NO_2] + k_3[NO_3] + k_D)$$

where C_0 is the initial count rate at the conclusion of the flash. For each experiment the empirical first-order rate constant $1/\tau$ was obtained by least-squares as the initial slope of a plot of $\ln C$ vs time. From the measured concentration of N_2O_5 and NO_2 , the concentration of NO_3 before the flash was calculated from the equilibrium constant¹⁵ for the reaction



$$K = [NO_2][NO_3]/[N_2O_5] \quad (9)$$

If atomic oxygen was produced from the photolysis of NO_3 , the initial concentration of NO_3 was calculated by difference. In any case a small correction term for the effect of NO_3 was calculated for each run, and a plot of $1/\tau - k_3[NO_3]$ against $[NO_2]$

$$(1/\tau - k_3[\text{NO}_3]) = k_1[\text{NO}_2] + k_D \quad (10)$$

gave k_1 as the slope and k_D as the intercept. A linear least-squares analysis of the complete data set of 144 pseudo first-order rate constants gave the following values and standard deviations

$$k_1 = 1.033 \pm 0.008 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (11)$$

$$k_D = 102.7 \pm 8.4 \text{ s}^{-1}$$

These studies were carried out under 14 different experimental conditions, and the 144 data points involve replication of conditions. For each of the 14 different conditions the results are averaged and listed in Table 1. A graphical display of the precision of (7) in fitting the data is given by a plot of $(1/\tau - k_3[\text{NO}_3] - k_D)$ vs $[\text{NO}_2]$ in Figure 1 for the 14 averaged results. The slope is k_1 .

4. Discussion

The rate constant k_1 found here is 10 percent higher than the currently recommended value,¹² which is based on several recent determinations^{2,10,11} (compare Equation 2). The estimated¹² uncertainty of k_1 is 10 percent. Even so, the significantly higher rate constant observed here calls for a careful consideration of possible systematic errors in this study or in the previous studies. This Discussion is concerned exclusively with this question.

As noted above, the calibration factor F , Equation (6), cancels, and any error in it will not affect the value of k_1 , so long as the concentration of atomic oxygen is directly proportional to count rate. The

maximum concentration of atomic oxygen in these experiments was 3×10^{11} molecules cm^{-3} , which is within the linear regime for resonance fluorescence of atomic oxygen.⁹ The initial concentration of atomic oxygen varied by a factor of 20 among these experiments, and there appears to be no correlation of the rate constant with initial concentration of atomic oxygen.

The absolute calibration of nitrogen dioxide concentration is crucial to the value of k_1 . The steps taken to establish this value were described in the Experimental section above. The standard deviation of the calibrations was less than 2 percent. Although attention was given to avoiding systematic error, one can never be certain that such errors are absent.

Radiation from the lamp that excited the resonance fluorescence of atomic oxygen was partially absorbed by the system, resulting in a small heating effect. The dissociation of N_2O_5 , Equation (8), has a strong temperature dependence, and more NO_2 could be expected when the lamp is on during a run than when it is off. During runs, the NO_2 detector came after the photolysis cell, and this effect is included in the observations. The magnitude of this effect was examined by observation of NO_2 with and without the lamp in operation. At the lowest concentration of NO_2 where N_2O_5 was present, a 10 percent increase in NO_2 concentration was detected. If the lamp caused a locally high concentration of NO_2 in the region of observation of resonance fluorescence, as opposed to a spatially uniform or time-delayed increase in NO_2 , the measured rate constant would be too high. For cases where the concentration of NO_2 exceeded 8×10^{13} molecules cm^{-3} , the lamp heating caused less than a 2 percent increase in NO_2 concentration. To test the effect of this local

heating, the 34 data points with the concentration of NO_2 greater than 8×10^{13} were separately used to evaluate the rate constant, and the value was

$$k_2 = 1.02 \pm 0.02 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (12)$$

which is in satisfactory agreement with the value obtained from all of the data, Equation (11). Furthermore, the values of k_1 obtained from pure NO_2 in N_2 (see the arrow on the abscissa of Figure 1) agree quite well with those from systems including the temperature sensitive N_2O_5 . This effect does not seem to be large enough to account for a significant error in the measured rate constant.

The measurement of time is based on the multichannel analyzer, and its absolute calibration was determined as a part of this study.

The microwave discharge could produce Lyman- α radiation from trace impurities of water or hydrocarbons in the helium gas, and although it is difficult to conceive of how atomic hydrogen might be produced from the photolysis of NO_3 by visible light, possible effects of Lyman- α radiation were checked by carrying out some experiments with MgF_2 windows, which pass Lyman- α radiation, and some with CaF_2 windows, which block this radiation. There were no differences in the observed rate constants.

In chemical kinetic studies some of the largest systematic errors are caused by unrecognized side reactions, and considerations were given to such reactions here. There is not enough energy in the flash to produce excited electronic states of atomic oxygen, such as $\text{O}({}^1\text{D})$, and thus reactions of $\text{O}({}^1\text{D})$ or its products could not be occurring in this system. At 10 torr N_2 , the excited electronic states of NO_2 are quenched

at times short compared to the 20 μ s time bins of these experiments. The reactions of atomic oxygen with N_2O_5 ^{12,15,16} or with HNO_3 ^{12,17} are extremely slow and of no consequence here. The concentration of NO_2 was so low that the concentration of N_2O_4 in equilibrium with it was less, usually far less, than 0.1 percent, and thus N_2O_4 did not have a significant effect in this system. At the total pressure of 10 torr N_2 the reaction, $O + NO_2 + M \rightarrow NO_3 + M$, contributed less than 0.3 percent to the observed rate of decay of atomic oxygen.

Since no systematic errors could be discovered in these studies, it is appropriate to ask if there could be any advantages to this method compared to previous studies. One possible advantage of this method is that it employed a continuous flow of reactants so that nitrogen dioxide had a chance to equilibrate itself between the gas phase and the walls of the apparatus, and this study carried out in situ analysis for nitrogen dioxide. It appears possible that previous investigators lost some NO_2 to the surfaces of the apparatus, which would tend to give rate constants systematically low.

Acknowledgment

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng-48.

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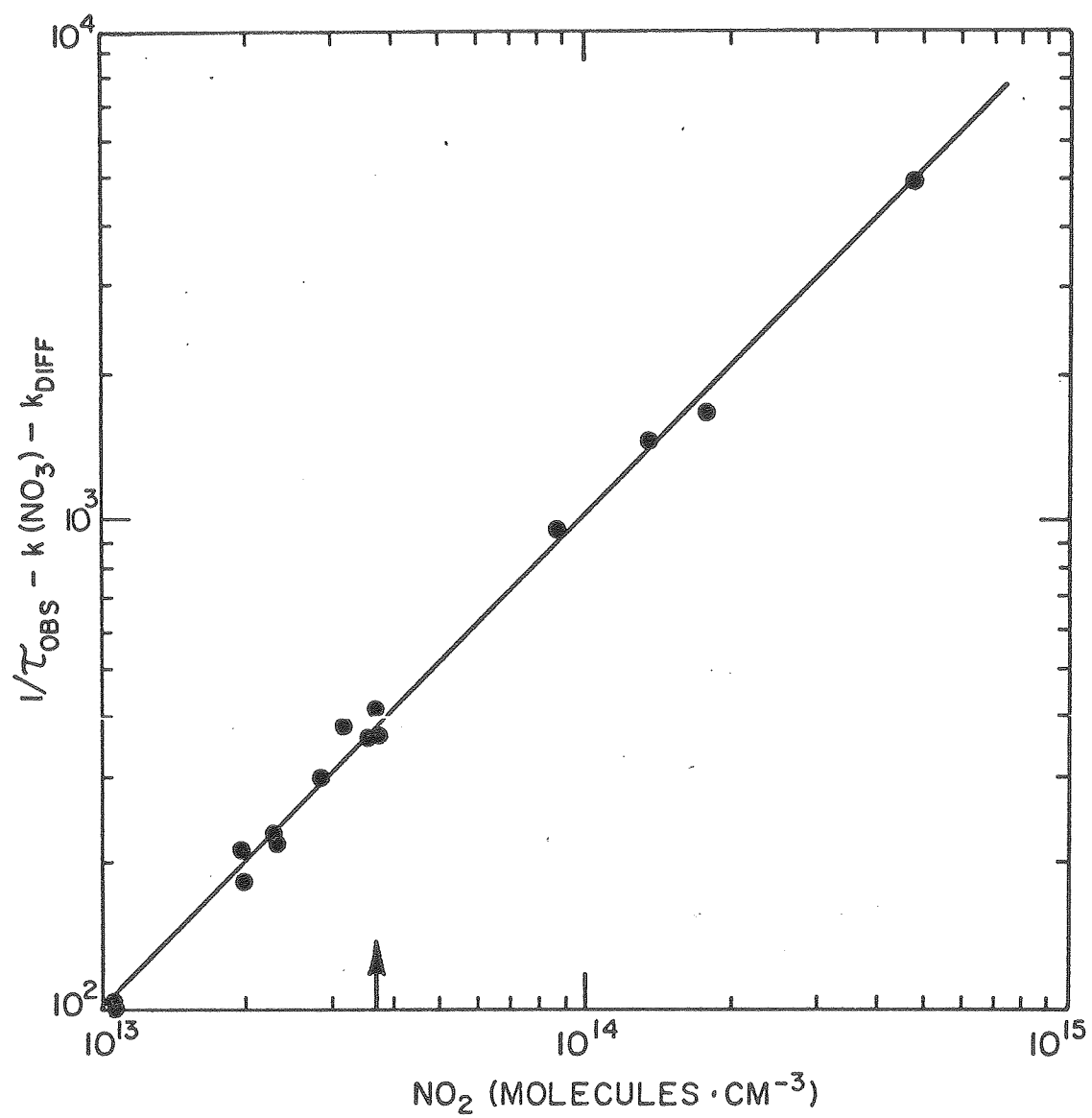
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Table 1. Clustered O + NO₂ Rate Data

$(1/\tau - k_3[\text{NO}_3]) \pm \sigma_y$ s ⁻¹	Average [NO ₂](molecules cm ⁻³) $\times 10^{-13} \pm \sigma_x$	Number of Data Points Averaged
1056 ± 3	8.69 ± .09	10
202.3 ± 10	1.05 ± .03	20
205.5 ± 5	1.05 ± .01	28
286.1 ± 8	1.98 ± .09	8
513.7 ± 5	3.70 ± .01	2
321.7 ± 4	2.30 ± .06	8
401.9 ± 40	2.84 ± .51	8
485.5 ± 33	3.17 ± .02	8
315.1 ± 16	1.98 ± .10	12
329 ± 4	2.29 ± .05	2
1544 ± 5	13.7 ± .14	16
460 ± 128	3.6 ± .12	16
5065 ± 159	47.9 ± .22	4
1777 ± 3	17.8 ± .02	2
		144 total

Figure Caption

Figure 1. Plot of $O + NO_2$ reaction rate vs NO_2 concentration at 296 K.



XBL799-7099